

Entropy Crisis, Defects and the Role of Competition in Monatomic Glass Formers

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Abstract

The demonstration here of an entropy crisis in monatomic glass formers along with previously known results finally establishes that the entropy crisis is ubiquitous in all supercooled liquids. We show that interactions that compete with crystal order weakens the ability to form glass. We also study the defects in the ideal glass; they are very different from those in the crystal.

A common feature of almost all materials is that they can become glassy, i.e. an amorphous solid, representing a *metastable* state [1]. The glass is obtained by cooling the supercooled liquid (SCL), and need not obey the third law of thermodynamics, which is only valid for equilibrium states [2]. The true equilibrium state corresponds to a crystalline state. The configurational entropy of SCL exhibits a rapid drop below the melting temperature T_M [1], and eventually vanishes at some temperature $T = T_K < T_M$. It will become *negative if extrapolated* to lower temperatures. Since a negative entropy is *unphysical*, an ideal glass transition must intervene to avoid this *entropy crisis* at T_K . In the limit of zero cooling rate (not accessible in experiments or simulations, but accessible in a theoretical setup) in the metastable region, metastable states become *stationary*, and can be described by "equilibrium" statistical mechanics by *restricting* the allowed microstates to be disordered; microstates leading to the crystalline state are *not* allowed. In experiments, the extrapolated configurational entropy of many glassy materials at $T = 0$ [3] is found to have a non-zero value depending on the rate of cooling. This does not rule out the possibility that the entropy of the hypothetical "stationary" glass vanishes in the limit of zero cooling rate at a non-zero temperature at a positive temperature.

Demonstrating an entropy crisis for supercooled liquids in a restricted formalism has been one of the most challenging problems in theoretical physics. An entropy crisis in long polymers was theoretically demonstrated almost fifty years ago by Gibbs and DiMarzio [4] to support the entropy crisis as a *fundamental principle* underlying glass transitions in long polymers. Their work was later severely criticized by Gujrati and Goldstein [5] for its poor approximation, and doubt was cast on whether the entropy crisis in long polymers was genuine. The situation changed when in a recent work, Gujrati and Corsi [6] established the existence of an entropy crisis in long polymers by using a highly reliable approximate approach. This was very important as the idea of Gibbs and Di Marzio has been pivotal in shaping our thinking about the ideal glass transition. Recently, we have also succeeded in demonstrating the entropy crisis in a dimer model [7] containing anisotropic interactions. However, to establish the entropy crisis as a fundamental principle underlying the glass transition in *all* supercooled liquids, we need to demonstrate the crisis in simple isotropic fluids containing monatomic particles. So far, this has not

been feasible in any theoretical approach and is one of the outstanding theoretical physics problems for a complete understanding of glass transition.

Here, we establish an entropy crisis in monatomic systems, thereby finally succeeding in establishing the entropy crisis as a fundamental mechanism driving glass transitions in all supercooled liquids. Study of monatomic glass formers will allow us to obtain a better understanding of the glassy structure (defects therein) whose accurate representation remains still challenging. The slow relaxation [1] in SCLs is similar to that observed in ordinary spin glasses [8]. Therefore, it is not surprising that ordinary monatomic glasses have been traditionally modeled as spin glasses, whose important features are their geometrical frustration and competition. It is commonly believed that the competition and frustration play an important role in promoting the glassy behavior. We will also check this hypothesis in this work.

It should be noted that frustrated antiferromagnets (AF) and spin glasses do not usually possess long range order at low temperatures because of a highly degenerate ground state [9] and their glassy behavior is brought about by the presence of frustration or quenched impurities and is somewhat well understood. In contrast, supercooled liquids require a *unique* ground state, the crystal. This distinguishes the glassy behavior in supercooled liquids and requires considering an *unfrustrated* AF model as a paradigm of simple fluids or alloys. We consider a pure (no frustration or quenched impurities) AF Ising model, which possesses a unique ordered state so that supercooling can occur. This then results in a glassy state. We are not aware of any simple model calculation to date to justify glassy states in a pure AF model. We also find that the competition considered in this work inhibits instead of promoting the glass transition, which is a surprising result.

Model. We introduce the following *AF Ising model* in zero magnetic field on a square or a cubic lattice (lattice spacing a) with the interaction energy

$$E = J \sum SS' + J' \sum SS'S'' \quad (1)$$

The first sum is over nearest-neighbor spin pairs and the second over neighboring spin triplets, which we take to be within a square for simplicity. We take $S = \pm 1$ to denote A, and B particles for an alloy, or the particle and void for a fluid. For $|J'| \leq 2J$, we have an AF ordering at low temperatures with a sublattice structure: spins of

a given orientation are found preferentially on one of the two sublattices. Antiferromagnetically ordered square (AFS) with spins alternating, and ferromagnetically ordered squares (FS) with spins the same are the only two square conformations that contribute to the first term in (1). We may identify the AF ordered structure as crystal [7]. For a fluid, this model represents a strong repulsion at a lattice spacing a , and attraction at lattice spacings $\sqrt{2}a$ between particles. For $|J'| \geq 2J$, the AF ordering is destroyed at low temperatures; S is the same everywhere. We set $J=1$ to set the temperature scale and only consider $|J'| \leq 2J$. It is easy to see that the free energy depends on $|J'|$, not on its sign. In particular, the ground state energy per spin of the AF ordered state is $E_0 = -2J$, regardless of J' . In the following, we will measure the energy and the free energy with respect to the ground state to give the excitation energies. In this case, both will vanish at $T = 0$. The non-zero value of $|J'|$ creates a preference for the product $SS'S''$ in square to be of a fixed sign, which then competes with the formation of the crystal in which this product can be of either sign. A positive (negative) J' provides preference for $S = -1$ (+1), so J' can be used to also control the abundance of one of the spin states.

The entropy $S(T)$ of the model cannot be negative if the state has to occur in Nature or simulations; indeed, neither can ever show any entropy crisis. If the metastable state entropy $S(T) = 0$ at a positive temperature T_K , then its *extension* will experience an entropy crisis and must be replaced by an *ideal glass* below T_K , the *ideal glass transition temperature* [10]. The model cannot be solved exactly except in one dimension. It is usually studied in the mean-field approximation commonly known as the Bragg-Williams approximation [11] adapted for an AF case. However, the approximation is known to be very crude. Indeed, Netz and Berker [12] have shown that one of the shortcomings of the approximation is that it abandons the hard-spin condition $S^2 = 1$. This condition is easily incorporated in exact calculations on recursive lattices [13] and it was discovered that such calculations are more reliable than the conventional mean-field approximations. Therefore, we adopt the recursive lattice approach here.

We consider a homogeneous Husimi cactus in which q squares meet at a site. The model is solved exactly on the cactus as described in [13]. The cactus can be thought as an approximation of a square lattice for $q = 2$ or a cubic lattice for $q = 3$, so that the exact Husimi cactus solution can be thought of as their approximate solution.

Solution. We follow [13] and solve the model recursively. We label sites on the cactus by an index m , which increases sequentially outwards from $m = 0$ at the origin. We introduce partial PF's $Z_m(\uparrow)$ and $Z_m(\downarrow)$, depending on the states of the spin at the m -th cactus level. It represents the contribution of the part of the cactus above that level to the total PF. We then introduce the ratio

$$x_m \equiv Z_m(\uparrow)/[Z_m(\uparrow) + Z_m(\downarrow)], \quad (2)$$

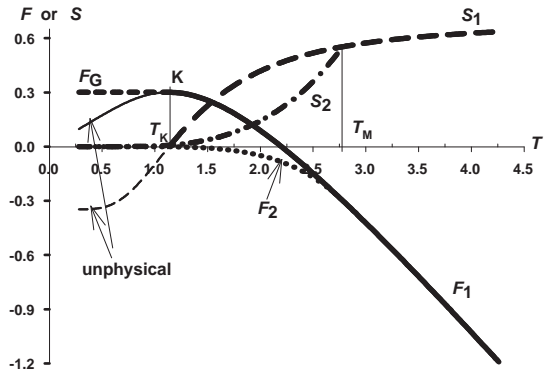


FIG. 1: The free energy and entropy for the two FP solutions. The model shows an entropy crisis and an ideal glass transition at T_K . The thin curves represent unphysical states (negative entropy) and are replaced by the ideal glass state.

which satisfies the recursion relation (RR)

$$x_m \equiv \frac{f(x_{m+1}, x_{m+2}, v)}{f(x_{m+1}, x_{m+2}, v) + f(y_{m+1}, y_{m+2}, 1/v)}, \quad (3)$$

where $f(x, x', v) \equiv x^{2r}x'^r/uv^2 + 2x^rx'^ry^rv + x^{2r}y'^rv + ux'^ry^{2r} + 2x^ry'^ry'^r + y^{2r}y'^r/v$ with $r = q - 1$ and where $u \equiv e^{4\beta}$, $v \equiv e^{2\beta J'}$, $y \equiv 1 - x$, $y' \equiv 1 - x'$.

There are two kinds of fix-point (FP) solutions of the RR (3) that describe the bulk behavior [13]. In the 1-cycle solution, the FP solution becomes independent of the level m , and is represented by x^* . For $J' = 0$, x^* is given by $x^* = 1/2$, as can be checked explicitly. For $J' \neq 0$, $x^* \neq 1/2$ and has to be obtained numerically. This solution *exists* at all temperatures $T \geq 0$; thus, there is no spinodal of this solution. This solution describes the disordered phase. At $T \rightarrow \infty$, all spins are uncorrelated so that the density per site $\phi_{FS} = 1/8$, and $\phi_{AFS} = 1/16$, and the entropy is $S = \ln 2$. As T is reduced, ϕ_{FS} decreases, while ϕ_{AFS} increases. The other FP solution of interest is a 2-cycle solution associated with the AF state containing AFSs [13]. It alternates between two values x_1^* and x_2^* which occur at successive levels. This kind of FP solution has also been observed in other systems such as semi-flexible polymers [6, 14], dimers [15], and stars and dendrimers [16], and has been thoroughly investigated. At $T = 0$, the 2-cycle solution is given by $x_1^*, x_2^* = 1, 0$ or $0, 1$ describing the perfect crystal ($\phi_{FS} = 0, \phi_{AFS} = 0.5$). This solution then evolves with T due to excitations and describes the crystal at low temperatures. The free energy is calculated by the general method due to Gujrati [6, 13, 16]. Whichever solution has the lower free energy represents the equilibrium state. The solution with the higher free energy, then, represents the metastable state, which can only be observed in Nature if its entropy remains non-negative. The temperature where the two solutions have the same free energy is the transition temperature, which we denote by T_M .

Results. The results for $q = 2$ are presented in Figs.

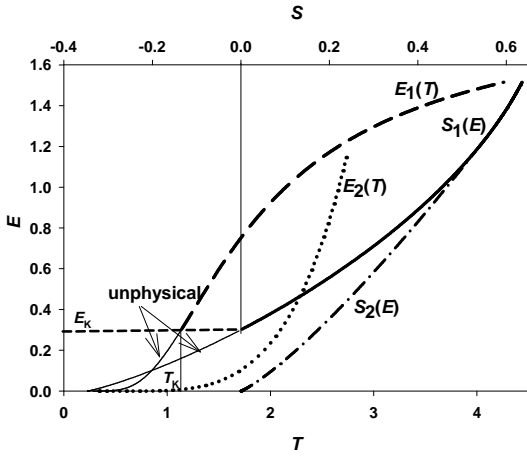


FIG. 2: $S-E-T$ relationship for the two FP solutions. The excitations in the two near $T = 0$ are very different. The excitations in the 1-cycle state near T_K are strongly interacting as opposed to those near $T = 0$.

1-3. The free energy F_1 and entropy S_1 associated with the 1-cycle FP solution are shown by the continuous and the long dash curves in Fig. 1. The free energy F_2 and entropy S_2 associate with the 2-cycle FP solution are shown by the dotted and the dash-dot curves. The energy $E(T)$ as a function of T and the entropy $S(E)$ as a function of E are shown in Fig. 2. We have set $J' = 0.01$ for figures 1, and 2. As said earlier, F and E represent the contributions of excitations with respect to the ground state energy $E_0 = -2J$, so that they vanish at $T = 0$, as is clearly seen in Figs. 1, and 2. The transition temperature is found to be $T_M \cong 2.7706$. We see from Fig. 1 that F_1 crosses zero and becomes positive below $T = T_{eq} \cong 2.200$ but again becomes zero (not shown here, but we have checked it) as $T \rightarrow 0$. Thus, F_1 possesses a maximum at an intermediate temperature (see point K in Fig. 1) at $T = T_K \cong 1.1316$, so that the entropy S_1 vanishes there. Below T_K , the *continuation* of F_1 and S_1 , shown by their thin portions in Figs. 1 and 2, continue to satisfy the *stability condition* (non-negative specific heat). Despite this, they *cannot* represent any physical states in the system due to *negative entropy* and have to be discarded as *unphysical*. Below T_K , we must extend the metastable state (described by F_1 and S_1 between T_K and T_M) by a glassy phase of a constant free energy $F = F_G$, see the short dash horizontal line in Fig. 1, and $S = S_G = 0$. The 1-cycle energy at K is $E_{1K} = F_G \cong 0.301$. The entropy S_2 is never negative, and the 2-cycle FP solution represents the equilibrium crystal below T_M .

Competition with Crystal Ordering. The behavior as a function of $|J'|$ of the transition temperature T_M (empty circles), the ideal glass transition temperature T_K (filled circles) and their ratio T_M/T_K (triangles) are shown in Fig. 3. As said above, $|J'|$ competes with

the crystal ordering and reduces T_M . One can use the inverse ratio T_K/T_M as a *measure* of the relative ease of glass formation: larger this value, easier it is to obtain the ideal glass as T_K is not too deep relative to T_M . What we observe is that T_M/T_K increases with $|J'|$, with T_K approaching zero faster than T_M , so that the ratio T_M/T_K continues to increase with $|J'|$. This implies that it becomes harder to obtain the ideal glass as T_K becomes relatively farther away from T_M as $|J'|$ increases. The competition provided by $|J'|$ weakens not only crystal ordering but also "weakens" forming the ideal glass. Consequently, competition does not enhance the ability to undergo ideal glass transition, an interesting result which is being explored further [17] to see if other competitions behave similarly.

Analysis of Defects. To understand the difference between the disordered liquid and the crystal defects, we turn to Fig. 2 and observe that near $T = 0$, the excitation energies of both FP solutions are very different, even though $E_1(0) = E_2(0) = 0$. Detailed analysis will be presented elsewhere [18]. The excitations (defects) in the crystal are known to be due to *point-like* excitations caused by the reversal of a single spin which changes the free energy by $\cong 8J$ (coordination number 4) with respect to the ground state; here we assume J' to be small. Therefore, this excitation causes the leading term in the free energy F_2 to be $1/u^2$ [19] and can be treated as *non-interacting* as long as they are small in number. What kinds of excitations are deducible from the form of F_1 near $T = 0$? To answer this, we consider the simple case of $J' = 0$, which also gives rise to F_1 over the entire temperature range $T \geq 0$. Here, we can carry out an analytical investigation since $x^* = 1/2$. As we are only interested in the excitation energy, we will overlook the unphysical nature of the entropy near $T = 0$ to study the excitation spectrum. The excitation energy $[=4(\phi_{FS} - \phi_{AFS})+2]$ and free energy are given by ($w = 3 + u/2 + 1/2u$)

$$E_1(T) = -(u - 1/u)/w + 2, F_1(T) = -(T/2) \ln w + 2,$$

where $\phi_{FS} = 1/4uw$, and $\phi_{AFS} = u/4w$. The entropy is calculated using $S_1(T) = (E_1 - F_1)/T$. At $T = 0$, $E_1(0) = 0$ implies that all squares are. Near $T = 0$, we find that $E_1(T) \cong 12/u$, $F_1(T) \cong T(\frac{1}{2} \ln 2 - 3/u)$ and $S_1(T) \cong -\frac{1}{2} \ln 2 + 3/u + 12\beta/u$. (S_1 at $T = 0$ in Fig. 1 is almost $-\frac{1}{2} \ln 2$.) What we discover is that the excitations due to $1/u$ -term near $T = 0$ are not the *uncorrelated* single spin reversal in the background of a perfect crystal. Rather, they represent *correlated* excitations in the form of FS in the background of AFSs by turning an AFS into a FS. Each FS excitation requires an energy $4J$ per site. This is in accordance with the general discussion above. Indeed, the excitation spectrum is given by the expansion of $E_1(T)$ in powers of $1/u$ [19]. These excitations also explain why the thin portion of $E_1(T)$ rises more rapidly than $E_2(T)$ in Fig. 2 so that $E_K \cong 0.3$ is appreciably higher than the $E_2(T) \cong 0.1$ at T_K due to a lower $\phi_{AFS} \cong 0.426$ and higher $\phi_{FS} \cong 3.58 \times 10^{-4}$ in the metastable state. In contrast, $\phi_{AFS} \cong 0.498$, and $\phi_{FS} \cong 7.991 \times$

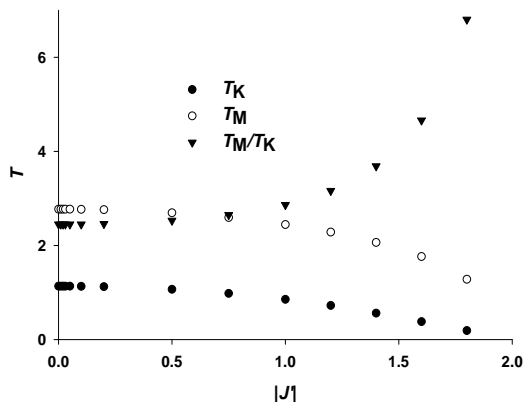


FIG. 3: The effect of $|J'|$, which creates competition with the crystal ordering, on T_M , and T_K and their ratio. The weakening of crystal ordering also "weakens" the ideal glass formation.

10^{-7} in the crystal. This is consistent with most defects in the crystal being point defects. As there is no non-analyticity at T_K in SCL, the excitation spectrum remains continuous above T_K where physical states occur. The density of sites ϕ_{unc} not covered by AFSs and FSs is $\phi_{\text{unc}} \simeq 0.148$ in SCL and $\phi_{\text{unc}} \simeq 3.684 \times 10^{-3}$ in the crystal. These sites are probably uncorrelated in SCL, but this needs to be carefully checked. Nevertheless, the above analysis leads us to conclude that the excitations at or above T_K in SCL are very different from the point defects of the crystal and are the ones that get frozen in the glass that is formed at T_K . For $T < T_K$, we have an ideal glass, shown by the horizontal short dash curve in Fig. 2, of constant energy E_K and zero entropy.

The excitation spectra of both solutions over the physical range are completely described by their respective entropies $S_1(E)$ (the thick part) and $S_2(E)$ shown in Fig. 2. For $E < E_K$, the excitations in the glass cannot change

since they are frozen at constant energy E_K , but continue to change in the crystal. In experiments, the ideal glass will never be observed due to time-limitations and one would obtain a non-stationary state whose entropy $\tilde{S}_1(E)$ must satisfy $\tilde{S}_1(E) \leq S_1(E)$ according to the law of increase of entropy [2]. In this case, the non-stationary glass will have some excitations at low temperatures.

For the AF case that we consider here, the 1-cycle solution is found to exist at *all* temperatures and describes the disordered liquid above and its metastable continuation below the transition temperature. There is no singularity in this fix-point solution at the transition. In contrast, for the ferromagnetic case ($J < 0$), the 2-cycle FP solution is never stable, and the 1-cycle solution has a singularity at the ferromagnetic transition and its entropy never becomes negative.

We have already shown elsewhere [15] that the glassy state for dimers contains a higher density of voids than the corresponding crystal at the same temperature. This is also true in the current model. The voids distribute themselves in the lattice at equilibrium, and the corresponding 1-cycle solution gives rise to an excitation spectrum so that $S_1(E)$ vanishes at T_K . If it happens that the system is quenched, then all we can say is that the corresponding spectrum $\tilde{S}_1(E)$ of the quenched system must satisfy the standard condition $\tilde{S}_1(E) \leq S_1(E)$. Despite this, it is possible that the entropy of the quenched system does not vanish at a positive temperature. There is no contradiction.

To summarize, our model calculation demonstrates that monatomic systems also give rise to an ideal glass, thereby making the entropy crisis ubiquitous. The glass contains correlated defects that are very different from those in the crystal. Moreover, the competition does not enhance the ability to form a glass. We have only investigated a classical model and it would be interesting to see if quantum calculations support this picture.

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